CHIN. PHYS. LETT. Vol. 26, No. 11 (2009) 117504

Effect of Temperature on Structural and Magnetic Properties of Laser Ablated Iron Oxide Deposited on Si(100)

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(Received 20 April 2009)

We fabricate Fe_3O_4 thin films on Si(100) substrates at different temperatures using pulsed laser deposition, and study the effect of annealing and deposition temperature on the structural and magnetic properties of Fe_3O_4 thin films. Subsequently, the films are characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM) and vibrating sample magnetometery (VSM). The XRD results of these films confirm the presence of the Fe_3O_4 phase and show room-temperature ferromagnetism, as observed with VSM. We demonstrate the optimized deposition and annealing conditions for an enhanced magnetization of 854 emu/cm^3 that is very high when compared to the bulk sample.

PACS: 75. 70. −i, 75. 79. −v, 75. 60. −v, 07. 55. Jg, 07. 70. Ds

It is well known that properties of Fe_3O_4 thin films are strongly dependent on crystal structure and growth conditions. As far as the magnetic properties of iron based compounds are concerned, Fe_3O_4 and γ-Fe_2O_3 are ferrimagnetic, Fe is ferromagnetic, and α-Fe_2O_3, FeO are antiferromagnetic.[1] Fe_3O_4 has been predicted to possess half-metallic properties with high spin polarization (100%) of the charge carriers at the Fermi level. Furthermore, it has a relatively high Curie temperature (860 K).[2] Several half metallic materials like half Heusler alloys (NiMnSb),[3,4] full Heusler alloys (Co_2MnSi),[5,6] chromium dioxide (CrO_2),[7,8,9] pervoskites ($La_{0.7}Sr_{0.3}MnO_3$),[10,11] and magnetite (Fe_3O_4)[12,13] are known. Out of these materials, Fe_3O_4 is especially attractive because of its promising applications in spintronic devices, magnetic storage, and as a source of spin-polarized current injection.[14−18]

There is a growing amount of literature discussing the optimum growth and deposition conditions of Fe_3O_4 due to their immense technological importance. A number of deposition techniques have been used to grow Fe_3O_4 thin films on different substrates, at different working pressures and from different phases of Fe targets.[19−22] However, it is still difficult to grow them with well defined compositions and structures at room temperature (RT). Pulsed laser deposition (PLD) is considered to be one of the best techniques that allows controlled film growth at low temperatures. In PLD, formation of oxides is favored by the presence of small amounts of O_2 inside the deposition chamber. The oxygen while interacting with the ablation plume promotes incorporation into the growing film.[23] A few reports about the annealing effect on the structural and magnetic properties of Fe_3O_4 thin films[24−26] exist, but their import and potential still remain unclear. The present work focuses on the effect of annealing on the thin films and demonstrates the conditions under which increasing magnetization can be achieved.

In this study, we have fabricated Fe_3O_4 thin films on Si(100) substrates at different temperatures (from RT to 450°C) by pulsed laser deposition, and investigated the effect of annealing and deposition temperature on the structural and magnetic properties. Phase analysis of the films was carried out by x-ray diffraction with Cu K_α radiation. Grain size, lattice strain and lattice constants were measured by the Williamson–Hall plot,[27] assuming that the peak shapes are Lorentzian. Crystal structure determination was performed using the PowderX software.[28] Film thickness and magnetic properties were determined from scanning electron microscopy (SEM) and vibrating sample magnetometery (VSM) respectively.

The films were deposited on Si(100) substrates by ablating a commercially purchased Fe_3O_4 target having one inch diameter and 5 mm thickness. Before deposition, the Si(100) substrates were subjected to chemical cleaning using acetone and isopropanol in an ultrasound bath. The cleaned substrates were then pre-heated in the deposition chamber at 500°C for 30 min under a vacuum of 1×10^{-7} torr to remove oxides.

The deposition procedure lasted for 20 min. For different experiments, the substrate was kept at different temperatures from RT to 450°C. In each case, a background pressure of 10^{-6} torr was achieved after adjusting the oxygen flow rate to 0.2 sccm. The pulse repetition rate, energy density of the Nd:YAG laser (Ekspla NL-303) and the target from substrate distance were set at 10 Hz, 1.3 J/cm^2 and 35 mm, respectively. The laser wavelength was 266 nm.

Subsequent to deposition, film thickness was deter-

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mined using scanning electron microscopy (SEM) (Hitachi S-4800). Furthermore, the RT deposited films were annealed at 350, 400 and 450°C for 1 h in base pressure of 1×10^{-6} torr. The crystalline structure and phases were determined by x-ray diffraction (XRD) (Rigaku D/Max-Rc MPA) using Cu K_α radiation. Finally, the RT magnetic properties were measured by vibrating sample magnetometry (VSM) (Ricken Denshi, Japan).

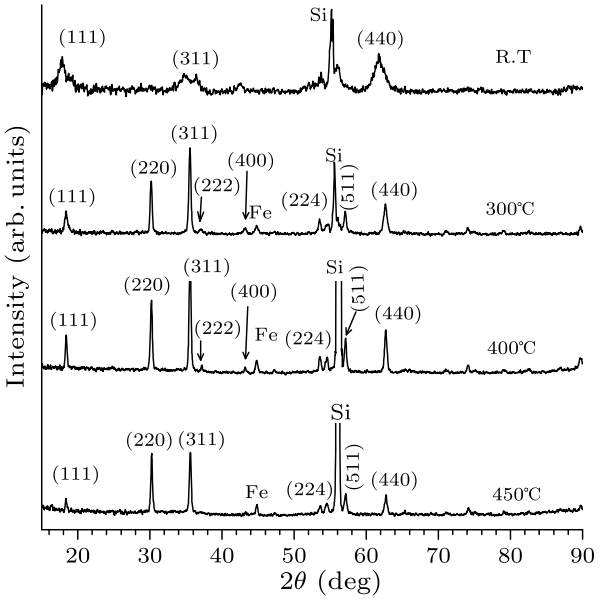


Fig. 1. X-ray diffraction patterns of Fe_3O_4 thin films on Si(100) substrates deposited at room temperature and annealed at the shown temperatures.

Figures 1 and 2 show the $\theta-2\theta$ scan XRD patterns of Fe_3O_4 thin films from RT to 450°C on Si(100) substrates. The lattice parameters were calculated using PowderX software.[28] The grain size and lattice strains were calculated from the Williamson–Hall plot and the equation,[29]

$$B\cos\theta = k\lambda/L + S\sin\theta,$$

where B represents the full width half maximum, L is the volume averaged grain size, k is the Scherrer constant, in our case taken to be 1, S is the lattice strain, and λ is the wavelength of Cu K_α radiation.

As the annealing temperature was raised from 300°C to 450°C, the diffractograms provide evidence of single phase polycrystalline Fe_3O_4 thin films, except for an α-Fe peak, the peak intensity being approximately 10% of the intensity of the strongest Fe_3O_4 peak. The crystallinity of the films increases with the increasing annealing temperature and the peaks became sharper, showing, as expected, that the grain size increases with the increasing annealing temperature.

The peak positions also shift to higher angles as compared to bulk Fe_3O_4. This shifting is related to uniform lattice strains in the plane of the films[29] compared to the bulk sample. The situation was, in fact, different for different deposition temperatures. The as-deposited films show smaller lattice strains as compared to annealed films due to the larger film thickness. When the thickness is larger, the strain effect due to substrate is minimized, explaining the reduction in strain with increasing deposition temperatures. However, the trends in the unit cell and crystallite size are identical in the annealed and as-deposited films. The results are presented in Tables 1 and 2. The increasing trend for the crystallite size has also been reported by Tangel *et al.*[30] and Parames *et al.*[31] The increasing trend of the lattice strain with the annealing temperature appears counter-intuitive as one expects annealing to result in reduced strains. In fact, the strain depends on two parameters, one is the ratio of the lattice constants of the substrate and the film and the second is the ratio of the coefficients of thermal expansion (α) for the substrate and the film. In our case, the second factor is the more dominant. The coefficient of thermal expansivity for Fe_3O_4 is $10.4\times10^{-6}\,K^{-1}$ (at 300°C)[32] and is four times the coefficient for Si, $2.6\times10^{-6}\,K^{-1}$. This means that Fe_3O_4 expands more than the Si substrate as the annealing temperature is increased, resulting in increased lattice strains.

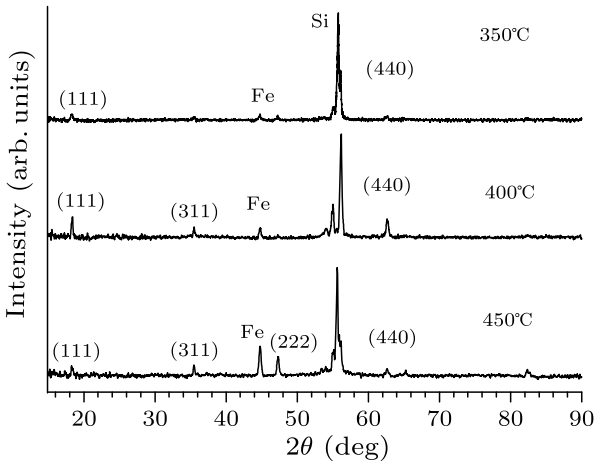


Fig. 2. XRD diffraction patterns of as deposited thin films. The deposition temperatures are also shown.

Table 1. XRD and VSM analysis of annealed Fe_3O_4 thin films on Si(100) substrates.

Annealing temperature (°C)	Lattice constant a (Å)	Lattice strain S	Estimated crystallite size (nm)	M_s (emu/cm^3)	H_c (Oe)
300	8.375	0.012	26.5	431	422
400	8.369	0.017	77.0	649	390
450	8.361	0.027	184.9	854	325

Table 2. XRD and VSM analysis of as-deposited Fe_3O_4 thin films on Si(100) substrates.

Depositing temperature (°C)	Lattice constant a (Å)	Lattice strain S	Estimated crystallite size (nm)	M_s (emu/cm^3)	H_c (Oe)
350	8.369	0.0035	18	374	449
400	8.364	0.0011	22	231	318
450	8.348	0.0010	30	477	274

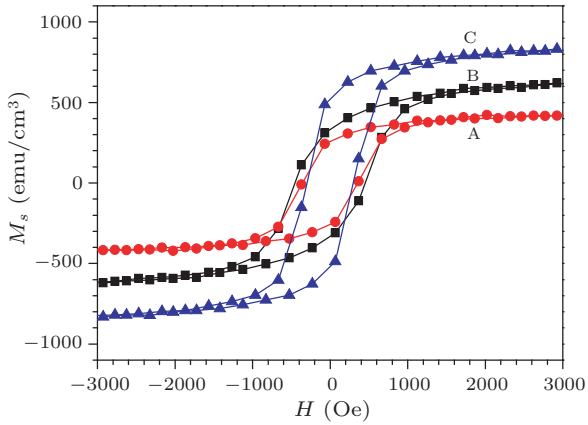


Fig. 3. In-plane magnetization curves of annealed thin films with A, B and C representing the samples annealed at 300, 400 and 450°C.

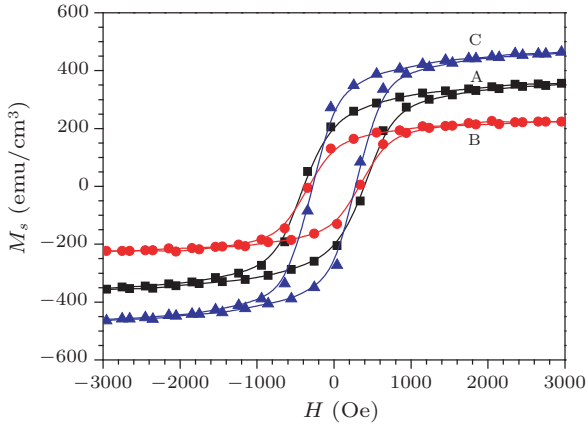


Fig. 4. In-plane magnetization curves of as-deposited thin films with A, B and C representing the deposition temperatures of 350, 400 and 450°C.

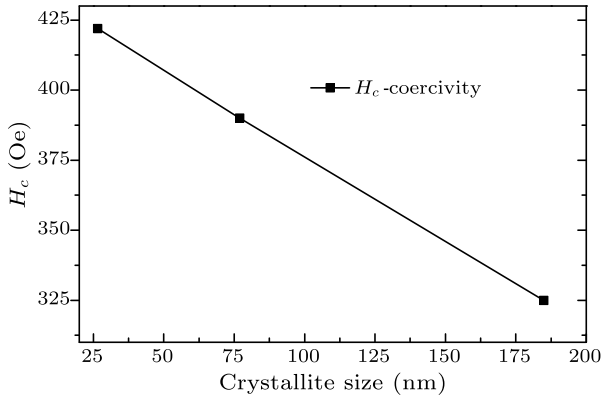


Fig. 5. Variation of H_c with crystallite size of annealed thin films.

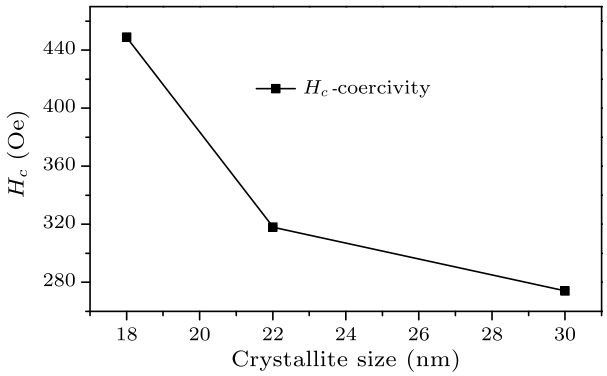


Fig. 6. Variation of H_c with crystallite size of as-deposited thin films.

Figures 3 and 4 show the RT. magnetization hysteresis behavior of annealed and as-deposited samples. The figures clearly show hysteretic behaviour suggesting their RT ferromagnetic property. The variations of coercivity H_c(Oe) with grain size are shown in Figs. 5 and 6. The saturation magnetization M_s and coercivity H_c as a function of annealing and depositing temperature (for both the annealed and as-deposited samples) are also summarized in Tables 1 and 2. In both the cases the coercivity decreases with an increasing annealing temperatue, deposition temperature and crystallite size. At an annealing temperature of 450°C, we obtain an unusually high saturation magnetization $M_s = 854\,\text{emu/cm}^3$ as compared to the bulk magnetization of Fe_3O_4 single crystals ($471\,\text{emu/cm}^3$).[33] Kennedy and Stampe have also reported a high saturation magnetization for the magnetite thin films grown on Si(100) substrate.[34] These authors used Fe as the target material and suggested that the increasing saturation magnetization could be due to the increasing Fe content in the thin films, which, due to its amorphous structure, does not appear in their XRD results. In our XRD patterns, sharp peaks for crystalline Fe become visible in the region of $2\theta \approx 45°$. The enhanced magnetization is very likely due to the presence of iron-rich centers. The hysteretic loops, apparently, indicate a single phase magnetic material but it is possible that the coercivity of the Fe is much too small (as compared to the $M-H$ loop step size) to distinctly make an appearance in the $M-H$ loop. In such a case, we cannot expect the hysteresis loop to confirm the synthesis of a single phase. Now there is the problem of the origin of Fe in the deposited films. It has been reported[35] that the stoichiometry of the iron oxide phase, i.e. the Fe:O ratio, depends on the growth conditions such as the

oxygen partial pressure, flow rate, laser fluence and substrate temperature. It is very likely that during deposition, phases of $Fe_{1-x}O$ (wustite) and hematite (Fe_2O_3) are also formed, which are reduced to Fe as annealing takes place under vacuum. For example, it has been demonstrated that FeO is stable only at a temperature greater than 570°C and is decomposed into α-Fe and inverse spinel Fe_3O_4 below 570°C.[36]

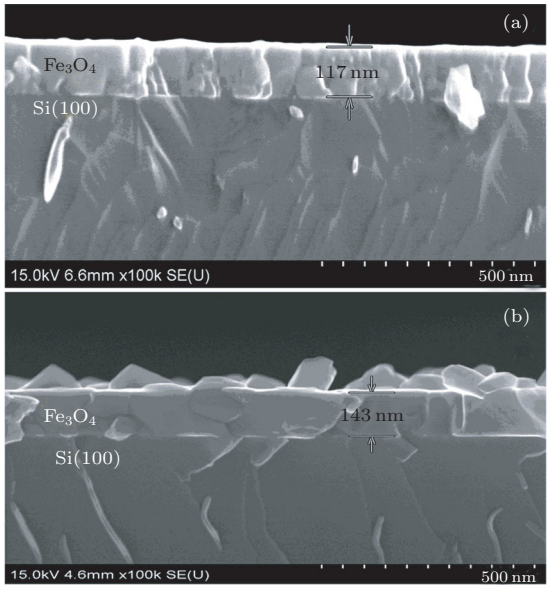


Fig. 7. SEM images of (a) Fe_3O_4 thin film annealed at 450°C and (b) as-deposited film at 450°C.

In summary, we have fabricated Fe_3O_4 thin films by PLD at different temperatures (from room to 450°C) on Si(100) substrates and studied the effect of annealing and depositing temperatures on the structural and magnetic properties of the Fe_3O_4 thin films. XRD patterns of both series show the cubic inverse-spinel structure with different orientations. Annealing increases the crystallinity of the samples. As far as the magnetic properties are concerned, we obtain the ferromagnetic behavior of all the thin films and obtain a surprisingly high magnetization of 854 emu/cm^3 at 450°C (annealed temperature) which is higher than the bulk value (471 emu/cm^3) of Fe_3O_4. This may be due to iron rich regions within the films as already reported. By increasing the annealing and depositing temperatures, the lattice parameters and coercivity decrease, while the volume average crystallite size increases.

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